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Improvements upon the continuum wavefunctions of Auger electrons by use of the least-squares variational method

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Abstract A variational least-squares technique is developed to obtain an iterative improvements upon the wavefunctions of Auger electrons emitted by the ion Ar^{2+} The core potentials seen by the Auger electrons are evaluated on the basis of the Hartree-Fock orbitals delivered by the conventional Hartee-Fock programs In order to illustrate our technique, the transition rates of the Auger electrons emitted from Ar corresponding to different configurations, namely $1s \rightarrow 3p\ 3p$, $1s \rightarrow 3s\ 3s$, $1s \rightarrow 2s\ 2s$, $1s \rightarrow 2p\ 2p$, $1s \rightarrow 2s\ 3s$ and $1s \rightarrow 2p\ 3p$ are calculated

Keywords Auger electrons, continuum wavefunctions, least-squares variational technique

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1. Introduction

In astrophysical and laboratory plasma and in surface science, various atomic processes are taking place, for example : electron – electron, electron – ion and ion-atom collisions. In electron-ion collisions, Auger electrons were first observed in 1925 by the French scientist Auger [1]. The Auger transition probability was formulated[2] by Wentzel (1927) and by Fermi (1956) which has also been discussed in the review article by Mc Guire [3]. Surface analysis based on Auger processes have been proposed and developed by many authors ; particularly, the significant experimental improvement by the Mehlhorn group[4-7] should be mentioned.

The application of Hartree-Fock[8] (HF) method to the determination of bound state wavefunctions is well known. In this method, the continuum wavefunction of the Auger electron can not be determined self-consistently because the continuum orbital is not square integrable. One possible way, in this method, to handle this problem (without extensive modifications of the program) is to assume a fictitious high Rydberg state of the same angular momentum, for

example $n_c \geq 6$ and $\ell c = \ell$, and run the HF program. This will produce a self-consistent [2] V_{HF} for 6 ℓc orbital ; these same potentials can then be used to solve for continuum wavefunction. To the extent that the 6 ℓc electron influences the other orbitals through screening, we have a set of wavefunctions which are equally distorted *via* the HF approximation ; the self-consistency is thus approximately satisfied by this procedure in so far as the continuum orbital is concerned.

On the other hand, trials to improve upon the continuum wavefunction were suggested by Colle *et al* [9] within the framework of the Schwinger variational method. Liegener, Abdel-Raouf and Ladik [10] formulated a variational least-square technique for calculating general non spherical continuum orbitals for Auger electrons emitted from macromolecules. The aim of the present work is to use this variational technique in order to improve the continuum wavefunction of Auger electrons produced by Ar. The real purpose of our calculations is to take the Auger electron as a free electron and not as an atomic electron in high rydberg state. This represents the real physical picture.

2. Theory

An excited ion or atom can stabilize by emission of Auger electron if : (a) A hole exists below at least two electrons (active electrons), (b) Energy lost when an electron fills the hole is enough to liberate the other electron to the continuum state, and (c) Parity must be conserved between the final state (f) and the initial state (i) Auger rates can be written as

$$A_a = \frac{2\pi}{\hbar} |< i | \frac{e^2}{r_{12}} | f >|^2$$

Or

$$A_a = \frac{2\pi}{\tau_0} |< i | \frac{1}{r_{12}} | f >|^2, \tag{1}$$

where τ_0 is the atomic unit of time $= \frac{\hbar a_0}{e^2} = 2.4 \times 10^{-17}$ sec., r_{12} is the relative coordinate of the two active electrons.

$$\frac{1}{r_{12}} = \frac{1}{|\bar{r}_1 - \bar{r}_2|} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} P_k (\cos\theta_{12}), \tag{2}$$

where $r <$ and r> are the smallest and largest of r_1, r_2 respectively, θ_{12} is the angle between r_1 and r_2 and P_k (Cos θ_{12}) is the Legendre polynomial which has the form (*e.g.* Weissbluth, 1978).

$$P_k (\cos\theta_{12}) = \frac{4\pi}{2k+1} \sum_{m=-k}^{k} Y^*_{Km} (\theta_1, \varphi_1) Y_{km} (\theta_2, \varphi_2) \tag{3}$$

where Y_{km} is the spherical harmonics and (θ_1, φ_1) are the polar angles of r_1. Eq. (1) may be written as

$$A_a (i \rightarrow f) = \frac{2\pi}{\tau_0} \left| \varphi_i (1) \varphi_c (2) \left| \hat{V}_{12} \right| \varphi_j (1) \varphi_k (2) \right|^2. \tag{4}$$

where $\hat{V}_{12} \equiv \frac{1}{r_{12}}$, is the electron-electron interaction operator, $\varphi_i(1)$ is the wavefunction of the bound state of the ion, $\varphi_j(1)$ and $\varphi_k(2)$ are the bound state wavefunctions of the two active electrons (obtained from HF-computer code, Ficher 1977), in the initial excited state and φ_c refers to the wavefunction of the continuum electron.

The exact continuum electron wavefunction $|\phi_c>$ has to satisfy the Schrödinger equation

$$(H-E)|\phi_c\rangle = |0\rangle, \tag{5}$$

where H and E are the total Hamiltonian and energy, respectively. The total Hamiltonian H is given by

$$H = \frac{-\hbar^2}{2m}\nabla_r^2 + V(r), \tag{6}$$

where $V(r)$ is the potential seen by the continuum electron at a distance r from the infinitely heavy nucleus of the considered atom. Thus, $V(r)$ has the form

$$V(r) = \frac{-Z_{eff}\ e^2}{\cdot} + V_c^q(r), \tag{7}$$

where $Z_{eff} = Z - N$ (Z is the nuclear charge of an atom q and N is the number of remaining electrons), $V_c^q(r)$ is a screening core potential defined by

$$V_c^q(r) = V_{c\ Coul}^q(r) + V_{c\ ex}^q(r), \tag{8}$$

$V_{c\ Coul}^q(r)$ and $V_{c\ ex}^q(r)$ are the Coulomb and exchange parts of the total potential. According to Abdel-Raouf[11], these potentials can be derived and having the following forms

$$V_{c\ Coul}^q(r) = \sum_{j=1}^{M^q} N_j^q \left\langle \Phi_j^q(r_i) \qquad\qquad \Phi_j^q(r_i) \right\rangle, \tag{9}$$

where M^q is the number of core orbitals of an atom or ion q and N_j^q is the number of electrons occupying the orbital j and each electron is at a distance r_i from the nucleus and $\Phi_j^q(r_i)$ is the wavefunction of the i-th electron in the orbital j. The prime on the sum sign means that the term -2 is repeated for each j. The exchange part of the core potential is defined by

$$V_{cex}^q(r) = -\sum_{j=1}^{M^q} \left\langle \Phi_c^q(r_i) \quad \frac{}{|r-r_i|} \quad \Phi_j^q(r_i) \right\rangle, \tag{10}$$

where c is employed for distinguishing the wavefunction of Auger electron (continuum electron). $|\phi_c\rangle$, in eq. (5), can be expanded by

$$|\phi_c\rangle = |S> + K_{11}|C> + |\phi\rangle, \tag{11}$$

where K_{11} is the tangent of the s-wave phase shift η_0, $|S>$ is the regular part and $|C>$ is the irregular part with an associated cut-off function for excluding the singularity at the origin and $|\phi>$ is a Hilbert-space wavefunction describing possible virtual states composed of the continuum electron and the ion. It is the superposition of bound state functions $|\chi_i>$ which go asymptotically to zero. Thus we have

$$|\phi\rangle = \sum^{n} d_i \, |\chi_i\rangle. \tag{12}$$

The least-squares variational method proceeds (Abdel-Raouf [12], 1984) by defining a trail wavefunction such that

$$\phi_c^{(n)} > = |S> + K_{11}|C> + \sum_{i=1}^{n} d_i \;\; \chi_i >. \tag{13}$$

The wavefunctions $|S>$, $|C>$ and $|\chi_i>$ of eq. (13) are chosen as

$$S = \frac{\sin(Kr)}{\sqrt{K}}, \; C = \frac{\cos(Kr)(1-e^{-\alpha r})}{\sqrt{K}} \text{ and } \chi_i = r^i e^{-\alpha r}.$$

The variational parameters K_{11} and d_i ($i = 1, 2, ..., n$) are determined by considering the following projections

$$\begin{aligned} &<S|H - E|\phi_c^n> = V_1, \\ &<C|H - E|\phi_c^n> = V_2 \text{ and} \\ &<\chi_i|H - E|\phi_c^n> = V_{i+2}, \quad i = 1, 2, ..., n. \end{aligned} \tag{14}$$

The V_i's are subjected to the following variational principle

$$\delta \sum^{n+2} V_i^2 = 0, \tag{15}$$

and the variational parameters are obtained by applying this variational principle. Thus, the final form of $\left|\phi_c^{(n)}\right\rangle$ can be written as

$$\left|\phi_c^{(n)}\right\rangle = \frac{1}{\Delta:n} \begin{vmatrix} |S> & |\chi_1> \ldots . |\chi_n> \\ M^s & \Delta:n \end{vmatrix} + K_1^n \begin{matrix} |C\rangle & |\chi_1> \ldots . |\chi_n> \\ M^c & \Delta:n \end{matrix} \tag{16}$$

where

$$M^{s} = \begin{bmatrix} (S:\chi_1) \\ (S:\chi_2) \\ \cdot \\ \cdot \\ \cdot \\ (S:\chi_n) \end{bmatrix}, \qquad M^{c} = \begin{bmatrix} (C:\chi_1) \\ (C:\chi_2) \\ \cdot \\ \cdot \\ \cdot \\ (C:\chi_n) \end{bmatrix}$$

and

$$\Delta:n = \begin{matrix} (\chi_1:\chi_1) & (\chi_1:\chi_2).....(\chi_1:\chi_n) \\ (\chi_2:\chi_1) & (\chi_2:\chi_2).....(\chi_2:\chi_n) \\ \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \cdot \\ (\chi_n:\chi_1) & (\chi_n:\chi_2).....(\chi_n|\chi_n) \end{matrix} \tag{17}$$

The matrix element $(f:g)$ is defined by $(f:g) = \sum_{k=1}^{n} (f/\chi_k)(\chi_k/g)$. Particularly, we have $|\chi_{-1}\rangle = |S\rangle$ and $|\chi_0\rangle = |C\rangle$, the χ_i's, $i \geq 1$, are the Hilbertspace wavefunctions defined above and *e.g.* $(f|\chi_i) = \langle f|H - E|\chi_j\rangle$.

It may be noted that the variational process can be carried out by assuming a certain form of $|\Phi_c\rangle$ appearing in eq. (10). It is suggested here to employ the continuum wavefunction used by the distorted wave approximation as the original Hartree fock wavefunction. This provides us with the first order iteration of $|\Phi_c\rangle$, eq. (16), and consequently the first order iteration of Auger transition rate, eq. (4). An iterative second order improvement upon the last $|\Phi_c\rangle$ can be achieved by introducing it into eq. (10), in order to obtain new set of values of the potentials $V(r)$ at all points of the space, and apply the above mentioned least-square variational technique. The new $|\Phi_c\rangle$ leads to a second order iteration of the transition rate, eq. (4). With the available computer facilities, we can calculate automatically higher order iterations.

3. Results and discussion

Our computational process started with the creation of the computer codes to realize our previous variational iteration technique (VIT) for the calculation of improved rates of Auger emission from arbitrary atoms or ions.

Our calculations are made by testing the VIT by increasing the number of iterations and we have obtained satisfactory convergence of Auger rates at the second iteration. We applied this VIT to the transitions corresponding only to the zero angular momentum quantum number (ℓc) of the continuum electron as a first treatment.

The results for the following Auger transitions $1s \rightarrow 3p\,3p$, $1s \rightarrow 3s\,3s$, $1s \rightarrow 2s\,2s$, $1s \rightarrow 2p\,2p$, $1s \rightarrow 2s\,3s$ and $1s \rightarrow 2p\,3p$ of Ar^{2+} which are corresponding to $\ell c = 0$ are displayed in Table 1.

Table 1. Auger transition rates for the decay processes from Ar^{2+} (lc = 0).

Transition	Original HF	LSVM	
		First iteration	Second iteration
$1s \rightarrow 3p\ 3p$	0.20452 (+12)	0 20208 (+12)	0.19301 (+12)
$1s \rightarrow 3s\ 3s$	0.65614 (+12)	0 63389 (+12)	0 63389 (+12)
$1s \rightarrow 2s\ 2s$	0 67113 (+14)	0 63127 (+14)	0 63127 (+14)
$1s \rightarrow 2p\ 2p$	0 30139 (+14)	0.29191 (+14)	0 29194 (+14)
$1s \rightarrow 2s\ 3s$	0 69633 (+13)	0 69861 (+13)	0.69861 (+13)
$1s \rightarrow 2p\ 3p$	0 41894 (+13)	0.41982 (+13)	0 41982 (+13)

(+a) means 10^{+a} and LSVM refers the Least Squares Variational Method

From the table, we come to the following conclusions : (i) Increase of the order of iteration causes, the convergence of the Auger rates. (ii) The convergence of our iterative Auger rates shows the stability of our variational iteration technique for improving the continuum wavefunction of Auger electrons emitted from atoms or ions.

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